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- USSR -

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ISOTOPIC OXYGEN EXCHANGE BETWEEN WATER AND CARBON DIOXIDE

Following is a translation of an article by M. Ya. Kats and F. S. Lapteva in Zhurnal Fizicheskoy Khimii (Journal of Physical Chemistry), Vol. XXXII, No. 4, Moscow, April 1958, pages 864-868.

Abstract

"An investigation has been made into the reaction kinetics of isotopic exchange between water and CO_2 when the predominant quantities of reactants (99%) are in different phases (water in the liquid phase and CO_2 in the gaseous), depending upon the CO_2 pressure (0.5-60 atm), the temperature (0-90° C) and the deuterium concentration."

The isotopic exchange of oxygen in the system $\text{H}_2\text{O}-\text{CO}_2$ has been studied by a number of authors (1-4). However, in connection with the development of a method for the isotopic analysis of water, it became necessary to study this reaction in case of high CO_2 pressures and different temperatures both in the system $\text{H}_2\text{O}-\text{CO}_2$ as well as in the system $\text{D}_2\text{O}-\text{CO}_2$, when the bulk of the CO_2 is present in a gaseous state, and not in solution.

In our experiments, a standard 2-liter cylinder was used as the reaction chamber. Standard carbon dioxide (see Note) and water, enriched with the heavy oxygen isotopes O-17 and O-18 and deuterium, were fed into this chamber. The latter was then placed into a water thermostat (Figure 1) and was rotated with a speed of 0.5 rpm; the area of contact between water and carbon dioxide was approximately equal to 1,000 sq. cm. After a certain period of time, the water was drained from the chamber and was subjected to an isotopic analysis. Since the original carbon dioxide was present in a state of isotopic equilibrium with natural water, as a result of the exchange, a portion of the O-17 and O-18 isotopes is transferred from water to CO_2 , and a reduction in the water density is observed. (Note: The carbon dioxide used in these tests, supplied by a dry ice manufacturing plant, did not contain any hydrogen-containing admixtures.)

The density increase, (see Note) of water is equal to the sum of the density increase $\Delta \rho / \rho$, caused by the presence of excess deuterium, and of the density increase $\Delta \rho' / \rho$, caused by the presence of the excess heavy oxygen isotopes O-17 and O-18:

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The isotopic exchange of oxygen in the system H_2O-CO_2 has been studied by a number of authors (1-4). However, in connection with the development of a method for the determination of water, it became necessary to study this reaction in case of high CO_2 pressures and different temperatures (0-90°C) and the deuterium concentration. The density increase of water, depending upon the CO_2 pressure (0.2-60 atm) and CO_2 in the gaseous phase, depending upon the CO_2 pressure (0.2-60 atm) and the temperature (0-90°C) and the deuterium concentration.

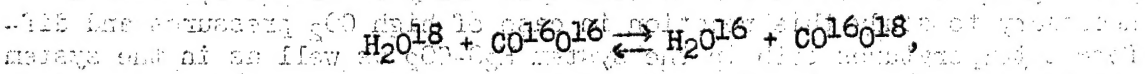
(Note: The density increase is the magnitude $\Delta \rho / \rho_0 = (\rho - \rho_0) / \rho_0$, where ρ_0 is the density of standard (natural) water, and ρ is the density of the water being tested.)

As a result of isotopic exchange, the density increase (or excess density) of water is reduced only at the expense of $\Delta \rho_K / \rho_0$. On the basis of the fact that, during a state of isotopic equilibrium, the excess amount of 0-17 and 0-18 isotopes, causing a density increase of oxygen in water $\Delta \rho_D / \rho_0$, must be distributed between water and CO_2 proportionately to the number of oxygen atoms, and taking the separation factor into account, the validity of the following relationship is clearly apparent (5):

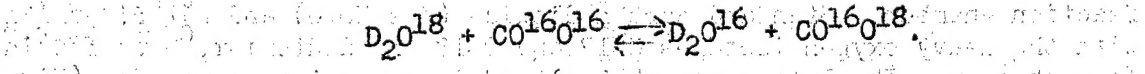
$$\frac{\Delta \rho_K}{\rho_0} = \left(\alpha_K \frac{M_P}{2MP_1} + 1 \right) \left(\frac{\Delta \rho}{\rho_0} - \frac{\Delta \rho_D}{\rho_0} \right) \quad (1)$$

where α_K is the separation factor of the 0-18 isotope between water and carbon dioxide; $\Delta \rho / \rho_0$ is the density increase of the original water; $\Delta \rho_D / \rho_0$ is the density increase after the reaction; P_1 is the weight of carbon dioxide, P is the weight of water; $M_1 = 44.01$, i.e., the molecular weight of carbon dioxide, $M = 18.02 + 18.68$, i.e., the molecular weight of the original water, whereby 18.02 is the molecular weight of natural water, and the factor 18.68 is calculated for a density increase $\Delta \rho / \rho_0$ at 25°C.

If we disregard the small effect exerted by the 0-17 isotope, we can assume that, in case of low deuterium concentrations in the water, the following main reaction takes place in the chamber:



while at higher deuterium concentrations, the following reaction takes place:



According to Yuri (Urey ?) (see [4]) and measurements performed by us at 90°C., the following value of α_K for the system H_2O-CO_2 can be assumed during calculations:

$$\alpha_K = \frac{[H_2O^{18}][CO^{16}_2]}{[H_2O^{16}][CO^{18}_2]} = 0.96,$$

The density increase of water, depending upon the CO_2 pressure (0.2-60 atm) and the temperature (0-90°C) and the deuterium concentration.

and for the system D_2O-CO_2 :

$$\alpha_K = \frac{[D_2O^{18}][CO^{16}O^{16}]}{[D_2O^{16}][CO^{16}O^{18}]} = 0.98.$$

Relation (1) is applicable only in case an isotopic equilibrium is established in the chamber. If, on the other hand, the duration of the reaction is shorter than the time required for the establishment of an isotopic equilibrium, formula (1) will yield lower $\Delta\rho_K/\rho_0$ density increase values. By determining $\Delta\rho_K/\rho_0$ values corresponding to different reaction times, we will obtain saturation curves, with the aid of which it is possible to determine the time at which an isotopic equilibrium was established in the chamber under given conditions. Experimental results are shown in Figures 2-4.

Density increases $\Delta\rho/\rho_0$ and $\Delta\rho'/\rho_0$ were measured by a differential picnometric method.

Effect of CO_2 Pressure. In plotting the curve shown in Figure 2, about 50 ml of water and the necessary amount of CO_2 were fed into the chamber under a corresponding pressure. An examination of this curve shows that, within the error range during measurements, the time at which an isotopic equilibrium is established in the chamber at $60^\circ C$. does not depend upon the CO_2 pressure within a 15-60 atm range.

At low pressures, the relative error occurring during measurements of the difference $(\Delta\rho/\rho_0) - (\Delta\rho'/\rho_0)$ is large, and for this reason the method of multiple washings was used for the same purpose. Preliminary tests have established that, at $90^\circ C$., a CO_2 pressure of 60 atm and about 50 ml of water, an isotopic equilibrium is established in the chamber after approximately 1.3 hours (Figure 4).

About 50 ml of water and CO_2 under a small pressure were fed into the chamber. The reaction took place at $90^\circ C$. during a period of 1.5 hours. The reacted gas was then removed, and the same amount of fresh CO_2 was introduced into the chamber. After several such reactions, the oxygen density increase in the water drained from the chamber was determined. Tests were conducted at a CO_2 pressure of 6 atm (2 tests), 3 atm (4 tests), 1.5 atm (7 tests) and 0.5 atm (10 tests).

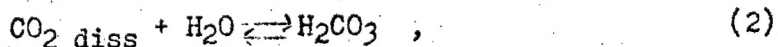
Within the measurement error limits, the oxygen density increase in water was found to be equal to the calculated density increase, assuming the establishment of an isotopic equilibrium in each reaction. Thus, the velocity of the isotopic exchange reaction in the system H_2O-CO_2 is not reduced when the CO_2 pressure is reduced from 60 to 0.5 atm, i.e. the process of oxygen isotope exchange is a reaction of the first order.

Effect of Temperature. In plotting the curves shown in Figure 3, about 100 ml of water and about 600 g of CO_2 were fed into the chamber. At 90, 60 and $40^\circ C$., the bulk of the CO_2 in the chamber was present in a gaseous state at a pressure of about 120, 110 and 100 atm (only 1% is

dissolved in water). At lower temperatures, a portion of the CO_2 in the chamber was also present in a liquid state (about 30% at 24° , about 58% at 12.5° and about 70% at 0°); the density of this liquid CO_2 is smaller than the density of water.

Effect of Deuterium Concentration. In plotting the curves shown in Figure 4, approximately 50 ml of water and about 300 g of CO_2 were fed into the chamber. The reaction was conducted at 90°C . The pressure in the chamber was equal to approximately 60 atm. Curve 1 was obtained with samples of water, in which the concentration of heavy oxygen isotopes was equal to 0.9 and 1.1%, while the deuterium concentration was respectively equal to 99.3 and 99.8%, i.e. this curve actually refers to a $\text{D}_2\text{O}-\text{CO}_2$ system. In this case, the isotopic equilibrium sets in after about 2 hours. Curve 2 was obtained with a sample of water, in which the concentration of heavy oxygen isotopes was approximately equal to 1%, while the deuterium concentration was also equal to about 1%, i.e. this curve actually refers to a $\text{H}_2\text{O}-\text{CO}_2$ system. In this case, the isotopic equilibrium is established after about 1.3 hours. Thus, the velocity of the isotopic reaction in the system $\text{D}_2\text{O}-\text{CO}_2$ is approximately 2 times smaller than in the system $\text{H}_2\text{O}-\text{CO}_2$.

It is known (3) that the velocity of the isotope exchange reaction between water and dissolved carbon dioxide is limited by the hydration and dehydration of carbon dioxide. In solutions with a $\text{pH} < 8$, the exchange is due mainly to the reaction:



while in solutions with $\text{pH} > 10$, it is due to the reaction:



At 25°C ., the half-period of reaction (2) is equal to about 17 minutes (the half-period of CO_2 dissolution in water is equal to 1 sec.). In our tests, the isotopic exchange was also influenced by reaction (2), but the exchange velocity must be smaller, since the bulk of the reacting media was present in different phases (water in the liquid phase, and CO_2 in the gaseous phase), and diffusion phenomena in both phases must have played a considerable role. In studies (2, 6), the isotopic exchange between 1.5 ml water and 16 ml CO_2 (or 5 ml water and 20 ml CO_2) at 25°C . and 1 atm was established by shaking the ampoule during a period of about 5 hours. In this case, 15-20% of the CO_2 was present in solution. In our tests (about 50 ml water and 300 g CO_2) at 24°C . and about 60 atm, the isotopic equilibrium was established in the course of 10-12 hours (Figure 3), which, apparently, is due to the fact that only about 2% CO_2 was dissolved in water.

In conclusion, in order to illustrate the fact that the density of water in our tests was reduced only as a result of an isotopic oxygen exchange, two washing curves might be mentioned. In plotting the curve shown in Figure 5, about 60 ml water and 300 g CO_2 were fed into the chamber during each test. As can be seen from Figure 5, the density increase of water drops sharply after the first washings, and then drops very slowly and in a linear manner as the number of washings was increased. Apparently, this linear section of the curve is due to the fact that the highly concentrated heavy water sample becomes diluted with natural water during the course of all manipulations performed during the washing process. The density increase, obtained by extrapolation towards the original sample in the linear portion of the graph, is caused only by the presence of deuterium. Figure 6 shows a similar washing curve obtained with a sample of water having a deuterium concentration only approximately 2 times greater than the deuterium concentration commonly found in nature, and in case of considerably higher ratio between the number of moles of water in the chamber and the number of moles of CO_2 in each reaction.

Conclusions

1. A study was made of the isotopic exchange reaction between water and CO_2 , when the bulk of the reacting compounds is present in different phases (water in the liquid phase, and CO_2 in the gaseous phase).
2. It was established that the velocity of the isotopic exchange reaction in the system $\text{H}_2\text{O}-\text{CO}_2$ is independent of the CO_2 pressure within a range of 0.5-60 atm.
3. The relation between the time at which an isotopic equilibrium is established in the system $\text{H}_2\text{O}-\text{CO}_2$ and the temperature in an interval of 0-90° C. was measured.
4. It was established that the velocity of the isotopic exchange reaction in the system $\text{D}_2\text{O}-\text{CO}_2$ is approximately 2 times smaller than in the system $\text{H}_2\text{O}-\text{CO}_2$.
5. It was demonstrated that an isotopic oxygen content in heavy water, even up to an ultimate (maximum) deuterium concentration, can be reduced to a normal oxygen content by means of an isotopic exchange reaction with CO_2 without the use of a catalyst.

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Figure Appendix

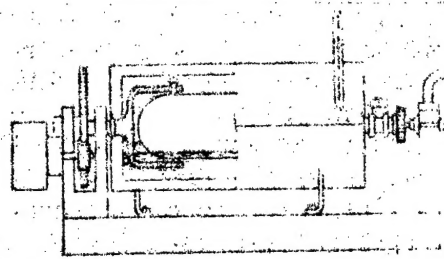


Figure 1

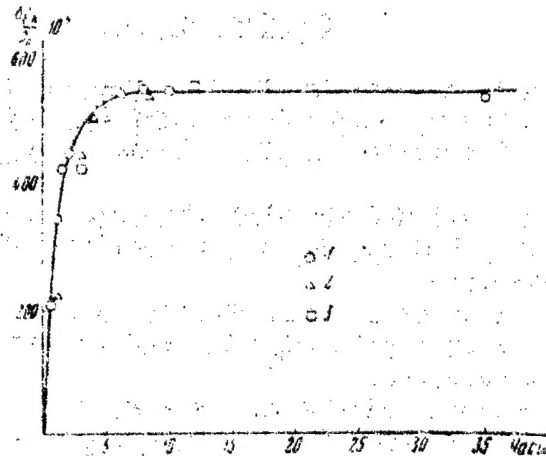


Figure 2

1 - 60 atm, 2 - 30 atm, 3 - 15 atm

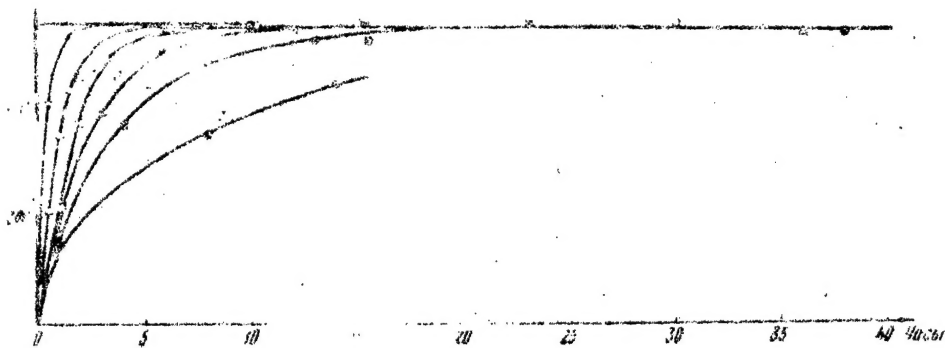


Figure 3.

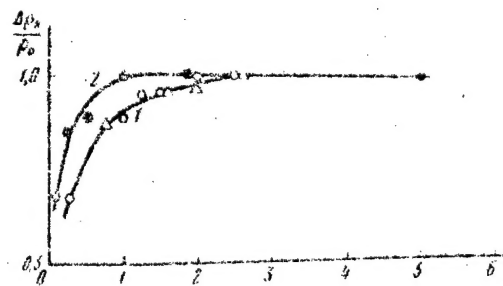


Figure 4

- 1 - For the system D_2O-CO_2
- 2 - For the system H_2O-CO_2

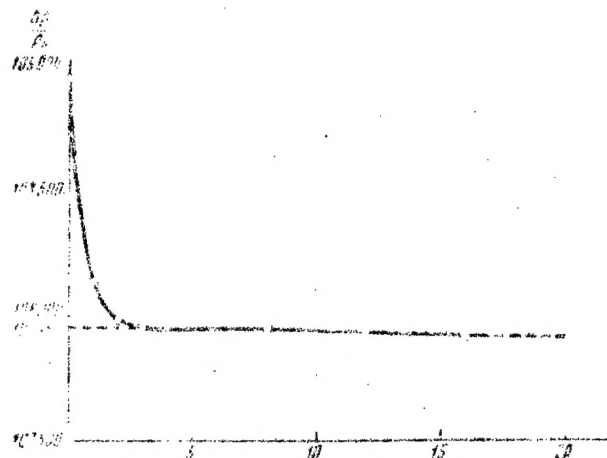


Figure 5
Relation between the density increase at 30° C and the number of washings, in a sample of water with an original deuterium concentration of 99.9%.
Abscissa: Number of washings

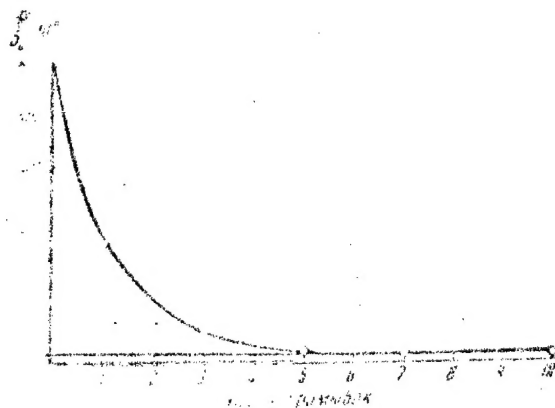


Figure 6
For a deuterium concentration of about 0.03%.
Abscissa: Number of washings

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